EFFECT OF DISSOLVED OXYGEN ON PHENOLS BREAKTHROUGH FROM GAC ADSORBERS

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ABSTRACT

This study demonstrates that molecular oxygen plays an important role in the adsorption of organic compounds from water by activated carbon. It was determined that the adsorptive capacity of granular activated carbon (GAC) for o-cresol can increase by almost 200% as a result of the presence of molecular oxygen in the test environment (oxic conditions). This increase in adsorptive capacity is not due to biological activity but can be totally attributed to the polymerization of o-cresol on the carbon surface under oxic conditions. The rate of adsorbate polymerization is such that the presence of molecular oxygen does not influence adsorption kinetics during the first 12 hours of adsorbent-adsorbate contact. However, the concentration of dissolved oxygen in the feed to a GAC adsorber can significantly influence the breakthrough of adsorbate. As the concentration of dissolved oxygen increased, more of this increased capacity is utilized during the early phase of breakthrough and, consequently, initial breakthrough is delayed. This phenomenon might completely change the existing procedures for the design and operation of GAC adsorbers in that it provides a competitive edge for adsorption as a treatment technology in water purification.

KEYWORDS

Adsorption; adsorptive capacity; molecular oxygen; breakthrough; phenolics

INTRODUCTION

Interest in removing biologically resistant organic contaminants from wastewaters has lead to increased application of activated carbon for waste purification. The adsorptive properties of activated carbon are defined by capacity, an equilibrium parameter, and by adsorption kinetics. The capacity of activated carbon for the retention of organic compounds is commonly expressed as an adsorption isotherm. The experimental protocol that is widely used for obtaining adsorption equilibrium data is the bottle-point technique. Unfortunately, a unique procedure for conducting this test has not yet been established. As a result, many different isotherms for the same adsorbate-adsorbent pair have been reported in the literature (Peel and Benedek, 1980). Theoretically, equilibrium values should
be independent of experimental protocol, and activated carbon capacities should be in agreement irrespective of the experimental procedure adopted.

Several researchers have reported discrepancies between the adsorptive capacities of activated carbon determined from isotherm tests and those obtained from batch and column studies. This was attributed to a continuously decreasing liquid phase sorbate concentration during the equilibration period (Yonge et al., 1985), irreversible adsorption (Yonge et al., 1985), decline in the intraparticle diffusion rate as saturation is approached during the later part of breakthrough (van Vliet et al., 1980), and the differences in diffusion processes occurring in macropores and micropores (Peel and Benedek, 1981; Seidel and Gelbin, 1986).

Different applications of activated carbon can cause the adsorption process to be carried out in the presence or the absence of molecular oxygen. Powdered activated carbon (PAC) used in the activated sludge process or GAC present at the inlet to an adsorber will remove organic compounds in the presence of molecular oxygen. On the other hand, in anaerobic GAC reactors, adsorption is carried out in the absence of molecular oxygen. Furthermore, biological activity in the carbon contactor or extensive bed depth can cause significant depletion of oxygen which will facilitate anoxic conditions. Therefore, it is very important to evaluate adsorptive properties under different environmental conditions that might occur as a result of the diverse applications of activated carbon. This study was undertaken to determine the effects of molecular oxygen on the adsorption of organic compounds.

**EXPERIMENTAL METHODS**

The effect of molecular oxygen on the adsorption process was studied using o-cresol as the adsorbate and 16x20 U.S. Mesh Filtrasorb 400 GAC (Calgon Carbon, Pittsburgh, PA) as the adsorbent. All adsorbate solutions were prepared using deionized water buffered at pH 7.0 with 0.01 M phosphate buffer. Prior to use, carbon was thoroughly washed with deionized water, dried at 105 °C, and stored in a desiccator until use. All the experiments described in this study were performed with the same batch of GAC.

Adsorbate concentration measurements were performed on a Hewlett Packard 8452A Diode-Array Spectrophotometer (Hewlett Packard, Palo Alto, CA, U.S.A.) at a wavelength of 269 nm. Concentration measurements were conducted using both 5 cm and 1 cm quartz cells.

**Adsorption Equilibrium** Many studies have been conducted to evaluate the effect of carbon preparation, size of carbon particles (pulverized or intact GAC), buffer application, initial sorbate concentration, and equilibration time on the adsorptive capacity of activated carbon for different organic compounds. There has also been considerable research on the nature of oxygen containing functional groups present on activated carbon surface and their influence on adsorption capacity. Coughlin and Ezra (1968) reported that oxidation of the surface of activated carbon increased the quantity of acidic oxygen resulting in diminished capacity of the carbon for phenol and nitrobenzene. Magne and Walker (1986) demonstrated that chemisorption of oxygen on activated carbon, at 573 K, caused a reduction in the initial capacity of carbon for the retention of phenol. However, the literature contains no references regarding the influence of molecular oxygen on the adsorptive properties of activated carbon.

Two different experimental procedures were used in this study to evaluate the influence of molecular oxygen on the adsorptive capacity of GAC for organic compounds. According to the first procedure, denoted henceforth as "oxic", accurately weighed portions of GAC (±0.1 mg) were placed into 160 ml bottles, to which 100 ml of an adsorbate solution was added. The bottles were then sealed with rubber stoppers and aluminium caps and placed on a rotary shaker. The headspace in each bottle was purged with pure oxygen thus providing ample quantities of oxygen needed to maintain fully oxic environment. Other sources of molecular oxygen in this procedure are: air associated with carbon...
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particles and the D.O. present in the water used for preparing the adsorbate solutions. According to the proposed experimental protocol, most literature experimental procedures for conducting isotherm experiments can be classified as oxic procedures since they usually facilitate the last two sources of oxygen.

The anoxic procedure, on the other hand, requires the total absence of molecular oxygen from the isotherm bottles. This was achieved by displacing the air associated with carbon particles with nitrogen gas, stripping the oxygen from the water with nitrogen prior to addition of sorbate and purging the headspace in the bottle, if any was used, with nitrogen gas prior to sealing. To ensure maximum displacement of the oxygen entrapped in the carbon pores, GAC was purged with nitrogen gas twice a day for 3 days. It is possible that not all the oxygen adsorbed on the surface of GAC can be removed just by purging with nitrogen gas. However, it was not the intention of this study to evaluate the effects of irreversibly adsorbed or chemisorbed oxygen on the capacity of GAC for o-cresol.

Each set of isotherm bottles included two blanks with no carbon to check for loss of adsorbate due to volatilization and/or adsorption onto the walls of the bottle. Prior to concentration measurements, liquid samples were filtered through 0.45 μm nylon filters (Micron Separation, Inc.) to prevent interference of carbon fines with spectroscopic analysis.

Samples of the activated carbon used in both experimental procedures were extracted in soxhlet extraction apparatus for one day with methanol followed by further extraction with methylene-chloride for an additional period of three days. Extracts of the carbons were analyzed by chromatographic separation on a 30-m DB-1 fused silica capillary column (J & W Scientific, Folsom, CA, U.S.A.) mounted on a Hewlett Packard 5890 Series II Gas Chromatograph equipped with a flame ionization detector (Hewlett Packard Co., Palo Alto, CA, U.S.A.). The purpose of these experiments was to determine the effect of different experimental procedures on the extraction efficiency for GAC. Gas Chromatographic/Mass Spectrometric analyses were also performed on these extracts.

Adsorption Kinetics The effect of molecular oxygen on adsorption kinetics was evaluated using data from two closed batch kinetic experiments conducted under oxic and anoxic conditions, respectively. Both experiments utilized the same initial adsorbate concentration (200 mg/L), the same concentration of activated carbon (500 mg/L), and identical mixing conditions. Oxygen was eliminated from the test environment from the anoxic batch test and enriched for use in the oxic experiment using approaches similar to those employed for the isotherm studies. Liquid samples (15 mL) were withdrawn periodically from the reactor over a period of 2 weeks. These tests were also used to determine the time needed for equilibration under the oxic and anoxic experimental conditions.

Column Studies o-Cresol breakthrough curves (BTCs) were obtained, using 1 in (2.54 cm) I.D. glass columns charged with 200 g of activated carbon. The initial o-cresol concentration was maintained at 50 mg/L for all column experiments. The feed solution to the columns was prepared using deionized water, buffered with 0.01 M KH₂PO₄ with the pH adjusted to 7.0 with NaOH. The adsorbers were operated in an upflow mode at a flow rate of 100 mL/min. This flow rate resulted in a hydraulic loading of 11.8 m/h and an empty-bed contact time (EBCT) of 4 min. Breakthrough experiments were conducted using different influent concentrations of dissolved oxygen (DO), namely 0.5, 4, 9, and 30 mg/L. The experiment where the influent dissolved oxygen concentration was maintained at 0.5 mg/L was conducted by stripping oxygen from the feed solution with nitrogen gas and keeping the solution under a headspace of nitrogen. Due to the fact that a total of 144 L of feed solution was pumped through the column per day, it was not possible to reduce the dissolved oxygen concentration to below 0.5 mg/L. The other influent dissolved oxygen concentrations, namely 4, 9, and 30 mg/L, were maintained using deionized water as produced in the laboratory, or by saturating the feed solution with air or pure oxygen.
RESULTS AND DISCUSSION

Adsorption Equilibrium Several oxic and anoxic adsorption isotherm runs were performed using the experimental conditions listed in Table 1. All the experimental data are presented in Figure 1.

Table 1. Experimental Conditions for o-Cresol Isotherm Tests

<table>
<thead>
<tr>
<th>Initial Concentration (mg/l)</th>
<th>Headspace Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 (2 runs)</td>
<td>Pure Oxygen oxic</td>
</tr>
<tr>
<td>150</td>
<td>Pure Oxygen oxic</td>
</tr>
<tr>
<td>100 (2 runs)</td>
<td>Pure Oxygen oxic</td>
</tr>
<tr>
<td>1000</td>
<td>Absent anoxic</td>
</tr>
<tr>
<td>1000 (2 runs)</td>
<td>Nitrogen anoxic</td>
</tr>
<tr>
<td>200</td>
<td>Nitrogen anoxic</td>
</tr>
<tr>
<td>150</td>
<td>Absent anoxic</td>
</tr>
<tr>
<td>50  (3 runs)</td>
<td>Nitrogen anoxic</td>
</tr>
</tbody>
</table>

Figure 1. Adsorption isotherms for o-cresol

The experimental data on the adsorptive capacity of F-400 for o-cresol were modeled very well by the Freundlich isotherm equation. Freundlich parameters K and 1/n were 241.3 ± 3.6 and 0.079 ± 0.003, for the oxic adsorption isotherm, and 94.14 ± 1.92 and 0.165 ± 0.004, for the anoxic case. Most of the isotherm data represent an equilibration period of two weeks while a few isotherm bottles from every set were allowed to equilibrate on the shaker for three and four weeks. Since there was no detectable
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removal of o-cresol from the liquid phase during the third and fourth week of the experiment, it was concluded that the period of two weeks is sufficient for equilibrium to prevail. The fact that there was no influence of the initial adsorbate concentration on the exhibited GAC adsorptive capacity substantiates this conclusion (Randtke and Snoeyink, 1980).

The presence of molecular oxygen had a major impact on the adsorptive capacity of GAC for o-cresol. For an equilibrium aqueous phase concentration of 1000 mg/L, the presence of molecular oxygen caused an increase in the GAC adsorptive capacity of 42% over the capacity that was attained under anoxic conditions. This difference was even more pronounced in the lower concentration range where, for an equilibrium aqueous phase concentration of 1 mg/L, the oxic adsorptive capacity was 2.56 fold the capacity obtained under anoxic conditions. Several isotherm experiments were conducted using autoclaved Milli-Q water (tap water purified by reverse osmosis, ion exchange, and GAC adsorption). This water was used to minimize the potential for biological activity to occur in the isotherm bottles. The occurrence of biological activity under oxic conditions was discarded as a possible explanation for the observed difference due to the following reasons:

1. dissolved organic carbon (DOC) measurements conducted on liquid samples at the end of isotherm experiments agreed extremely well with theoretical values computed from concentration measurements for o-cresol obtained by UV spectroscopy (DOC to o-cresol concentration ratio, measured on 28 samples randomly selected from different isotherm runs was 0.772 ± 0.032 while the theoretical value equals 0.779);

2. inorganic carbon did not increase during the equilibration period which would normally be expected as a result of biological activity under oxic conditions (inorganic carbon measured on these 28 samples after the equilibration period averaged 1.9 mg/L, while the inorganic carbon concentration in the stock solution was 1.8 mg/L);

3. spectroscopic scans of liquid samples at the beginning and end of isotherm runs agreed extremely well with those obtained for solutions prepared for the calibration of the instrument;

4. companion plate count studies conducted by Calgon Carbon (Pittsburgh, PA) on samples of GAC equilibrated by the authors under oxic and anoxic conditions with o-cresol revealed the absence of any microorganisms capable of degrading o-cresol.

The extraction efficiency of o-cresol obtained for the carbons used in the two different experimental procedures is plotted as a function of the equilibrium carbon loading in Figure 2. The extraction efficiencies obtained for the GAC used in the anoxic isotherm experiments averaged 90% and exhibited almost no dependency on the degree of adsorbate loading on the carbon, qe. On the other hand, only 12 to 33% of the adsorbed o-cresol was extracted from GAC used in the oxic isotherm experiments. Furthermore, the extraction efficiency was very dependent on the degree of adsorbate loading on the carbon. GC/MS analyses of the extracts from the GAC used in the oxic procedure revealed the presence of significant amounts of dimers, trimers, and even tetramers of o-cresol. The discovery of polymers of o-cresol suggested that some polymerization reactions are taking place on the surface of GAC in the presence of molecular oxygen. These polymerization reactions are responsible for the increased removal of adsorbate from the liquid phase under oxic conditions. The results from these experiments indicate that the surface of activated carbon plays a key role in promoting these polymerization reactions since no polymers were detected in the blanks that accompanied every set of isotherm bottles prepared according to the oxic procedure.

Adsorption Kinetics The initial phase (first 12 hours only) of batch tests conducted in the presence and absence of molecular oxygen is given in Figure 3. As is apparent from Figure 3, the presence of molecular oxygen in test environment had very little influence on the removal of adsorbate from the liquid phase during the first 12 hours of adsorbent-adsorbate contact. This could explain why accelerated mini-column tests and short isotherm experiments with powdered activated carbon give
Figure 2. Extraction efficiency for GAC used in two experimental procedures

Figure 3. Initial phase of closed batch kinetic experiments
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significantly lower adsorptive capacity of activated carbon than isotherm experiments conducted over longer periods of time using granular activated carbon.

The data in Figure 4 represent normalized aqueous phase concentrations of o-cresol that were collected from the two batch experiments over a period of two weeks. The concentration of o-cresol in the anoxic batch test reached equilibrium values very quickly after the initial phase. On the other hand, almost 12 days were required for the test conducted in the presence of molecular oxygen to reach stable levels. Keeping in mind the fact that the rate of polymerization decreases with an increase in the length of the polymer chains formed, it is possible that the liquid phase concentration achieved in the oxic test after two weeks was still not in equilibrium with the adsorbed phase of o-cresol. However, the oxic batch test was terminated after this period since no additional removal of o-cresol from the solution was detected by UV spectroscopy during the last four years of the experiment.

Figure 4. Closed batch kinetic experiments with o-cresol

Column Studies The dissolved oxygen concentration in the feed solution had a significant impact on the breakthrough of o-cresol from a GAC adsorber. This is best illustrated in Figure 5 which presents the data collected from four column tests conducted in the presence of different levels of dissolved oxygen in the feed solution. As the concentration of dissolved oxygen in the feed solution increased, more of this additional adsorptive capacity that results from the presence of molecular oxygen in the test environment was utilized in the early portions of an experiment. Consequently, the presence of molecular oxygen caused a delay in the initial breakthrough of o-cresol. This phenomenon became more pronounced with an increase in the concentration of dissolved oxygen in the feed solution. The adsorptive capacity of GAC in these adsorbers, as obtained by integrating the area above the breakthrough curves, is given in Table 2.
Figure 5. Effect of oxygen on breakthrough of o-cresol

Table 2. GAC Adsorptive Capacity in Different Adsorbers

<table>
<thead>
<tr>
<th>Column Run No.</th>
<th>DO (mg/L)</th>
<th>Capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>200.9</td>
</tr>
<tr>
<td>2</td>
<td>4.0</td>
<td>229.6</td>
</tr>
<tr>
<td>3</td>
<td>9.0</td>
<td>270.0</td>
</tr>
<tr>
<td>4</td>
<td>30.0</td>
<td>307.0</td>
</tr>
</tbody>
</table>

For an influent o-cresol concentration of 50 mg/L, the anoxic adsorption isotherm predicts GAC adsorptive of 179.5 mg/L while the oxic adsorption isotherm predicts a capacity of 328.7 mg/g. GAC adsorptive capacity exhibited in Column run No. 1 was 10% above the value predicted by the anoxic adsorption isotherm due to the fact that there was still 0.5 mg/L of oxygen present in the feed solution. On the other hand, the capacity of the carbon in Column run No. 4 was 6.6% lower than the value predicted by the oxic adsorption isotherm. This can be due to the fact that this experiment lasted 11 days while the kinetic tests indicated that this period might not be sufficient for the polymerization reaction to really exert its full influence on the removal of adsorbate from the liquid phase.

SUMMARY

This study demonstrates that activated carbon exhibits two very different adsorption capacities as a result of different environmental conditions that can prevail in adsorption isotherm experiments. The presence of molecular oxygen can cause an increase in the GAC adsorptive capacity for o-cresol of almost 200% when compared to the capacity that was attainable under anoxic conditions. Therefore,
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The presence of molecular oxygen also has a significant impact on adsorption kinetics as is demonstrated by the results of two batch experiments conducted in the presence and in the absence of molecular oxygen. The rate of o-cresol removal from the liquid phase was almost identical in both experiments during the initial 12 hours of adsorbent-adsorbate contact. After that, the liquid phase o-cresol concentration in the anoxic batch test leveled off at the value predicted by the anoxic adsorption isotherm. On the other hand, the concentration of o-cresol in the batch test conducted in the presence of molecular oxygen continued to drop, but at a very slow rate, and required almost 12 days for stable concentrations to be established.

The observed phenomenon was explained by the findings of the extraction experiments conducted on carbons that were used in both the oxic and anoxic isotherm experiments. It was demonstrated that some polymerization of o-cresol is taking place on the carbon surface in the presence of molecular oxygen and that these polymerization reactions are responsible for the increased removal of adsorbate from the liquid phase under oxic conditions.

The practical role of molecular oxygen in the performance of GAC adsorbers was evaluated by conducting breakthrough experiment with four GAC columns operated in parallel under the same hydraulic and adsorbate loading rates but using different dissolved oxygen concentrations in the feed solution. The concentration of dissolved oxygen in the influent stream significantly influenced the performance of these GAC adsorbers. As the dissolved oxygen concentration increased, more of this additional adsorptive capacity of the carbon was utilized in the early stages of column operation and the initial breakthrough was significantly delayed. This approach in the design and operation of GAC adsorbers might completely change the existing operating procedures and provide a competitive edge for adsorption as a treatment technology in water purification.

REFERENCES